LECTURE 10

Free Energy and Entropy

Bose condensation is a second order phase transition which can be described by the Ginzburg–Landau free energy. Before we do this, let me remind you what entropy and free energy are.

Suppose we have an isolated system with energy E. Let Ω denote the number of states of the system between E and $E + \delta E$. Then the entropy S is given by

$$S = k_B \ln \Omega \tag{1}$$

where k_B is Boltzmann's constant. Entropy is loosely thought of as the disorder or the number of active degrees of freedom of the system. The second law of thermodynamics tells us that an isolated system maximizes its entropy. If the system is not isolated and absorbs a tiny amount of heat dQ, its entropy increases by

$$dS = \frac{dQ}{T} \tag{2}$$

where T is the temperature. This gives a macroscopic thermodynamic definition of entropy.

The Helmholtz free energy F is defined by

$$F = E - TS \tag{3}$$

where E is the internal energy of the system. The free energy describes a system that has a fixed number of particles N that is in contact with a heat bath at temperature T. Such a system always wants to minimize its free energy. When $T = 0$, the system is in its ground state and entropy is not important. However, as T increases, entropy becomes more important and a system wants to maximize its entropy S in order to minimize its free energy. In terms of the partition function $Z = \sum_n e^{-E_n/k_B T}$ that we introduced in lecture 2,

$$F = -k_B T \ln Z \tag{4}$$

We saw in lectures 2 and 3 that we could get useful quantities like $< E >$ and $< n_s >$ by taking the appropriate derivatives of $\ln Z$. Similarly we can get useful thermodynamic quantities by taking derivatives of F. For example, the entropy is given by

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \tag{5}$$

where the subscript V means that the derivative is taken a fixed volume. The specific heat at constant volume is given by

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V \tag{6}$$

First and Second Order Phase Transitions

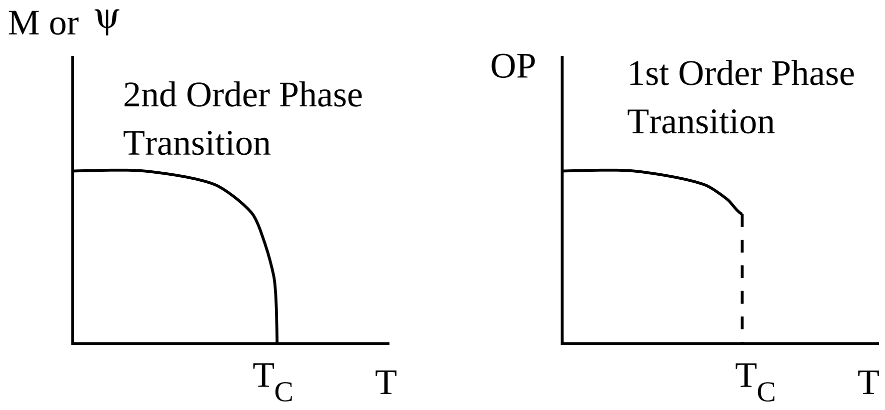
Phase transitions are often associated with ordering. For example the molecules in water are disordered whereas they are ordered in ice. This is a special case of a liquid–to–solid phase transition. Bose condensation is another example of a phase transition; the bosons are not coherent above T_C but a macroscopic fraction of them can be described by a coherent wavefunction ψ below T_C. There are 2 basic types of phase transitions: first order and second order. Water–to–ice (or liquid–to–crystalline solid) is an example of a first order phase transition. Typically a first order phase transition is associated with a discontinuity ΔS in the entropy. The entropy of the liquid S_ℓ is greater than the entropy of the solid S_s and $\Delta S = S_\ell - S_s$. The latent heat L is given by

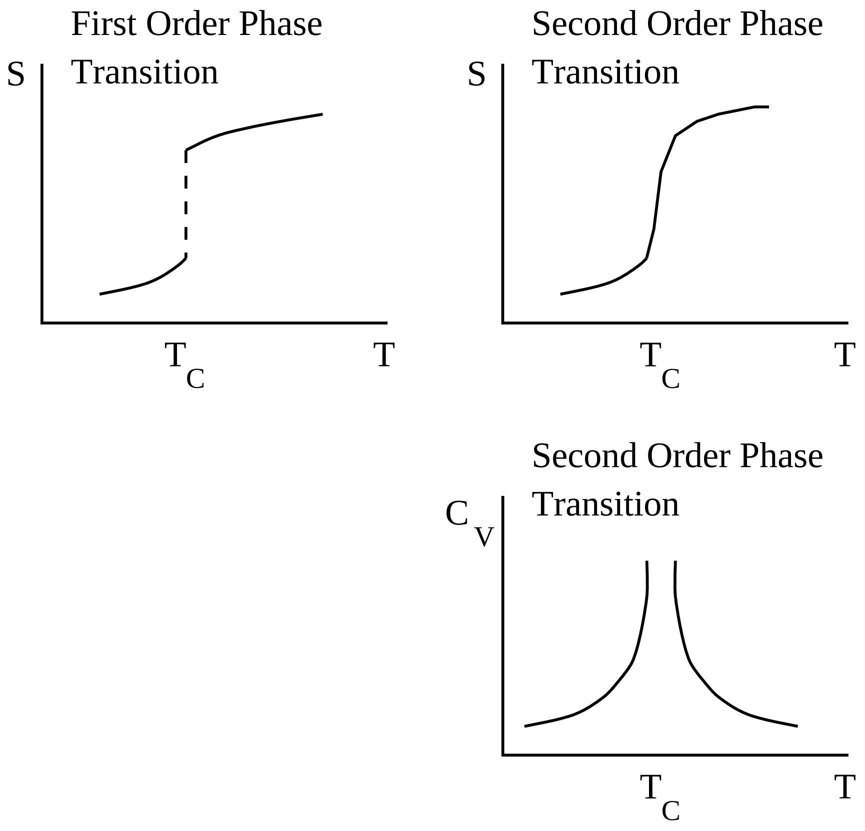
$$L = T\Delta S \tag{7}$$

To understand latent heat, suppose we add heat to a block of ice at a constant rate. Its temperature increases steadily until we reach 0 C, where the temperature stays put until the ice is all melted. All the heat we put in at 0 C goes into melting the ice; this heat is the latent heat of transformation. First order phase transitions are also often associated with sudden volume changes; ice expands relative to the water it came from. This is unusual; most solids take up less space than their liquid counterparts.

We often associate an order parameter with a phase transition. In a liquid the atoms or molecules are disordered in their arrangement, but at the transition, they suddenly become ordered. Thus a first order phase transition is associated with a discontinous jump in the order parameter.

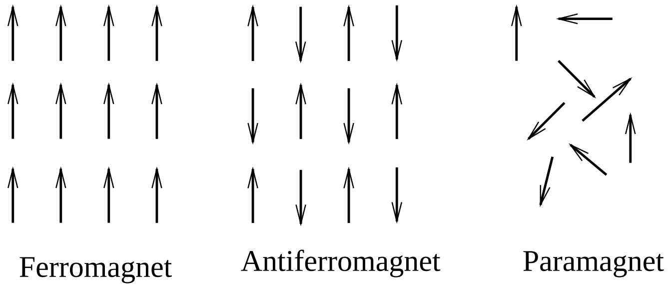
The other type of phase transition is a second order phase transition. Bose condensation is an example of a second order phase transition. A second order phase transition does not have any latent heat associated with it; the entropy is continuous at T_C. In a second order phase transition the order parameter grows continuously from zero as the temperature drops below T_C. For Bose condensation the order parameter is ψ; $\psi = 0$ for $T > T_C$ and ψ grows continuously as T decreases below T_C.





Another example of a second order phase transition is the paramagnetic to ferromagnetic phase transition. (Ferromagnets are bar magnets and can be found on refrigerator doors holding up notes.) We have discussed how the electrons in atoms have magnetic moments associated with them due to their spin and orbital angular momenta. When the atoms make up a solid, they can give the solid magnetic properties. If the magnetic moments are not pointing in any particular direction but can be aligned by an external magnetic field H_{ext}, then the system is paramagnetic with the magnetization $M = 0$. If the magnetic moments are lined up and are pointing in the same direction even when $H_{\text{ext}} = 0$, then the system is ferromagnetic with a net magnetization $M_z \neq 0$. (I'm calling $\hat{z}$ the direction of the magnetization.) A system at high temperatures can be in the paramagnetic state and can then undergo a second order phase transition into a ferromagnetic state at some temperature T_C. The order parameter is the magnetization M_z. It increases continuously from zero as T drops below T_C. One signature of the second order phase transition is a susceptibility $\chi(T)$ which diverges at $T = T_C$. Recall that $M = \chi H$. The susceptibility tells us how easy it is for the spins to respond to a magnetic field. $\chi(T)$ diverges as one approaches T_C from high or low temperatures.

As long as we're on the topic of magnetism, let me just mention one other kind of magnetic state, and that is the antiferromagnet. In an antiferromagnet the spins alternate in space: up, down, up, down, etc. The net magnetization is zero but the staggered magnetization, where we just look at every other spin, say, is not zero. This staggered magnetization is the order parameter. Like the ferromagnet, there is a second order phase transition from a paramagnet to an antiferromagnet. If you could put on a staggered magnetic field that alternated direction from site to site, you could measure a staggered susceptibility and this would diverge at T_C.



Broken Symmetry

Reference: P. W. Anderson, *Basic Notions of Condensed Matter Physics*, Addison–Wesley (1984), chapter 2.

There is one further concept that is associated with phase transitions and that is the concept of broken symmetry. Broken symmetry occurs when the ordered ground state does not have the full symmetry of the Hamiltonian. Recall that the symmetries of a Hamiltonian are associated with the operators that commute with the Hamiltonian. For example a homogeneous isotropic liquid has translational invariance; move all the atoms by the same amount and the liquid looks the same. The Hamiltonian describing this system is also invariant under translation. But once the system forms a crystal where the atoms or molecules sit on a periodic lattice, the translational invariance is broken and the ground state no longer has the full symmetry of the Hamiltonian. The Hamiltonian doesn't change; it still has translational symmetry, but the system it describes no longer has translation symmetry.

We can make this a bit more formal. Recall from lecture 2 that we said that if the Hamiltonian has translational symmetry, momentum is a good quantum number. States can be labelled by any value of the momentum. But in the crystal which is periodic and has discrete translational symmetry, the eigenstates are labelled by discrete values of the momentum. We saw an example of this in lecture 1 where we solved for the eigenstates of free particle system with periodic boundary conditions and found that only discrete values of the momentum were allowed.

Notice that this broken symmetry has a certain rigidity. If you push on one corner of the crystal, all the other particles move with it in such a way as to maintain their spatial relation with the corner that you are moving. True broken symmetry is associated with some type of rigidity. P. W. Anderson calls this generalized rigidity. (Photons in a laser don't have rigidity.)

Another example is the paramagnetic to antiferromagnetic transition. The Hamiltonian describing the spins and their interactions with one another is invariant under rotations in spin space. This means that we expect its eigenstates to have good total spin quantum numbers S and S_z.

$$H = J \sum_{i>j} \vec{S}_i \cdot \vec{S}_j \tag{8}$$

where the exchange constant $J > 0$. The paramagnet has the symmetry of the Hamiltonian. In other words if you rotate all the spins in a paramagnet by the same amount, the paramagnet will look the same. But if you rotate an antiferromagnet by an arbitrary angle, it looks different. So the antiferromagnet is a broken symmetry state. By this same argument, a ferromagnet is a broken symmetry state and is often cited as an example of broken symmetry. But technically speaking, it is not a broken symmetry state because a ferromagnet is an eigenstate of the Hamiltonian. It can be labelled by its total spin S and by S_z. On the other hand an antiferromagnet does not have a good spin quantum number S. The true ground state is a singlet with $S = 0$.

For the case of Bose condensation, the Bose condensed state is described by a wavefunction or order parameter $\psi = |\psi|e^{i\phi}$. The broken symmetry is gauge symmetry by which we mean that everywhere in the system the phase is ϕ. This is what gives the state macroscopic phase coherence. Note that this value of ϕ may fluctuate in time, but at any given time, it is the same everywhere.

When a continuous symmetry such as translation or rotation is broken, low energy excitations called Goldstone modes result. These low energy excitations are collective modes that involve perturbations related to the symmetry that was broken. Collective modes involve correlated motion among a large number of atoms or spins or whatever. For example, when translational symmetry is broken and a crystal results, small translations of the atoms back and forth result in lattice vibrations. These vibrations are the Goldstone modes and the Goldstone bosons are phonons. For an antiferromagnet where rotational symmetry is broken, the Goldstone modes are spin waves and the Goldstone bosons are magnons.

Broken symmetry is a deep and far ranging concept that applies to a wide variety of phenomena. Not only does it apply to phase transitions such as those involving Bose condensation, superconductivity, magnetism, and crystallization, but it also is important in understanding the Higgs mechanism in particle physics, and the formation of matter from energy in the early stages of the universe. Phase transitions have also been proposed to describe the origin of the universe: some think the big bang was a phase transition that involves symmetry breaking.

Ginzburg–Landau Free Energy

There is a very useful way to describe second order phase transitions using the Ginzburg–Landau free energy. Let's suppose we want to describe a second order phase transition where the order parameter is denoted by ψ. (We could just as easily use M if we were describing a magnetic transition.) We can write down a free energy in terms of ψ to describe the thermodynamics of the transition. Near the transition $|\psi|$ is small, so we can expand the free energy functional F in powers of $|\psi|$. We stop at fourth order. We only have even powers of $|\psi|$ because F must be invariant under the transformation

$\psi \to \psi e^{is}$ where s is a constant phase factor (or under the transformation $M_z \to -M_z$). Besides a cubic term $|\psi|^3$ would give a first order transition. So we can write

$$F = F_n + \int \left[\frac{\hbar^2}{2m^*} |\nabla\psi|^2 + a|\psi|^2 + \frac{1}{2} b|\psi|^4 \right] dV \tag{9}$$

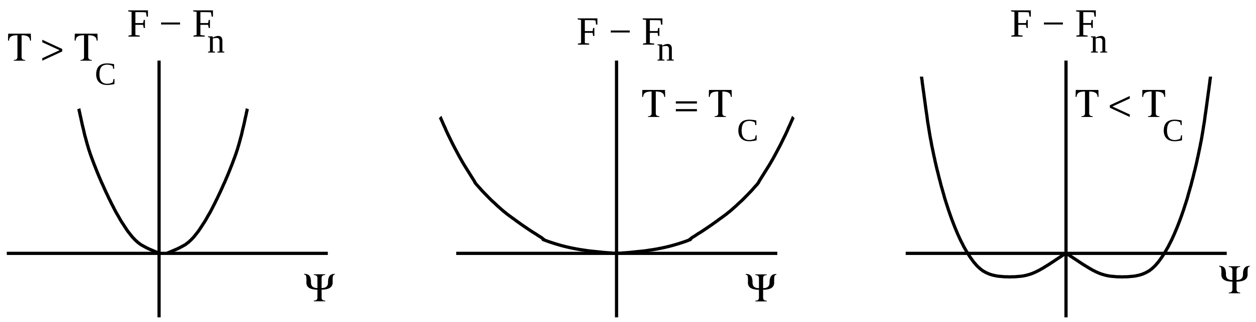
where V is the volume and F_n is the free energy of the normal state or high temperature state, e.g., the normal metallic state for a superconductor, the normal liquid helium state, or the paramagnetic state. a and b are coefficients. We have included a gradient term $|\nabla\psi|^2$. This tells us that the energy of the system increases if the order parameter varies in space. If it varies slowly so that there are only long wavelength fluctuations, then we can just keep the lowest order gradient terms. Let's assume the order parameter is uniform in space and get rid of this term entirely. This is fine for an isotropic homogeneous superconductor with no external field. The energy is lower that way and it makes life simpler. Now we just have a quartic polynomial in $|\psi|$. Because $|\psi|$ is independent of coordinates, we can pull it out of the volume integral: $\int |\psi|^2 dV = |\psi|^2 V$. Then we have

$$F = F_n + aV|\psi|^2 + \frac{1}{2} bV|\psi|^4 \tag{10}$$

The coefficient a is a function of temperature

$$a = \alpha(T - T_C) \qquad \alpha > 0 \tag{11}$$

Thus $a > 0$ for $T > T_C$ and $a < 0$ for $T < T_C$.



(The ψ axis should really be the complex ψ plane if ψ is the complex order parameter for a superfluid or a superconductor. If we had a complex ψ plane, then below T_C, $F(\psi)$ would have the shape of a Mexican hat or the bottom of a wine bottle.) For $T > T_C$, the equilibrium value of $|\psi| = 0$. For $T < T_C$, the equilibrium value of $|\psi|^2$ is given by

$$\frac{\partial F}{\partial(|\psi|^2)} = 0 \quad \Longrightarrow \quad |\psi|^2 = -\frac{a}{b} = \frac{\alpha(T_C - T)}{b} \qquad T < T_C \tag{12}$$

For a superconductor $|\psi|^2$ represents the density of superconducting electrons; for a superfluid or Bose condensate, it represents the condensate fraction. Notice that $|\psi|^2$

goes to zero linearly as the temperature approaches T_C from below. Substituting (12) back into equation (10) yields the value of the free energy F_s in the ordered state. The difference in the free energies of the normal and ordered states is

$$F_s - F_n = -\frac{a^2 V}{2b} = -V\left(\frac{\alpha^2}{2b}\right)(T_C - T)^2 \tag{13}$$

Using $C_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V$, we find that at $T = T_C$ there is a jump in the specific heat given by

$$C_s - C_n = V\frac{\alpha^2 T_C}{b} \tag{14}$$

Superconductivity

Superconductivity is in some ways like Bose condensation for fermions. All the electrons are in a single coherent state described by a wavefunction or order parameter $\psi = |\psi|e^{i\phi}$. Let's begin with a brief description of the normal metallic state which exists above T_C.

Normal Metallic State

Recall from lecture 7 that in a metal there are electrons which do not belong to any particular atoms or group of atoms but rather are delocalized and extended throughout the system. These are conduction electrons and carry the electric current when an electric field is applied. The atoms in a metal may also have core electrons which fill the inner shells and are local to each atom. We will ignore these core electrons since they don't affect the properties of the metal.

We will focus on the conduction electrons. For simplicity we can describe them as free electrons which fill the Fermi sea. To understand this, recall that in lecture 1 we found the eigenstates for a particle in a box with periodic boundary conditions. We found that the momentum acquires discrete values

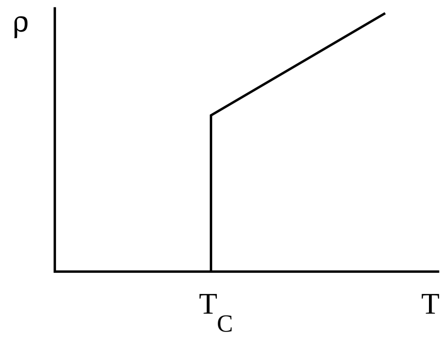
$$\begin{aligned} k_x &= \frac{2\pi}{L_x} n_x \\ k_y &= \frac{2\pi}{L_y} n_y \\ k_z &= \frac{2\pi}{L_z} n_z \end{aligned}$$

where the momentum $\vec{p} = \hbar\vec{k}$ and the numbers n_x, n_y, and n_z are any set of integers– positive, negative, or zero. We can imagine setting up coordinate axes k_x, k_y, and k_z and putting a point everywhere in $k-$space that there is an allowed state. Notice that as the size of the box gets bigger, the states get closer together in $k-$space. Since $E = \hbar^2 k^2/2m$, the lower energy states are the ones which are closer to the origin in $k-$space. Now let's put in our conduction electrons. We will fill the states in order of increasing energy. Only 2 electrons (spin up and spin down) can go into each state. After we've finished putting all our electrons into the states in $k-$space, we have what is called a Fermi sea. In our case the Fermi sea will be a sphere in $k-$space. The surface of this sphere is called the Fermi surface. The Fermi energy E_F is the energy of a state at the Fermi surface, and the Fermi wavevector k_F is the radius of the Fermi sea. So in our case $E_F = \hbar^2 k_F^2/2m$. An electron buried in the depths of the Fermi sea can't really jump to a nearby state in $k-$space because the nearby states are occupied. So these electrons don't contribute to the electric current. It's the electrons near the Fermi surface that can make transitions to unoccupied states above the Fermi surface and contribute to the electrical conduction.

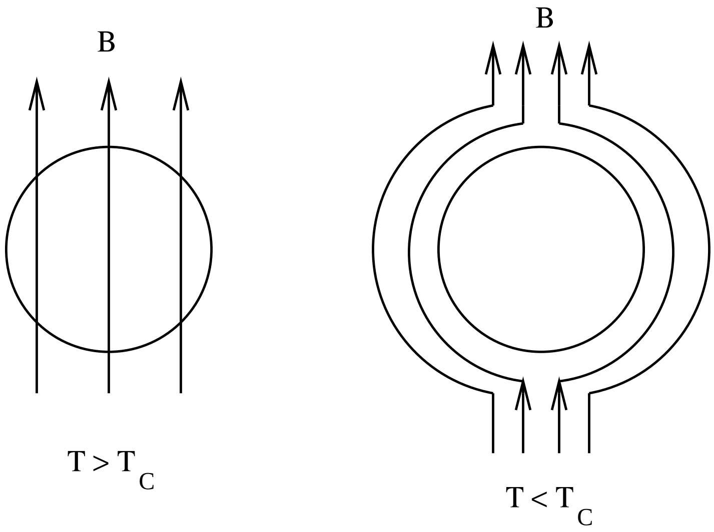
Superconductivity: Phenomenology

In 1911 H. Kamerlingh Onnes discovered superconductivity, 3 years after he had liquified helium. Many metals become superconducting below a critical temperature T_C. There are many experimental signatures of superconductivity. Let me list a few:

1. Infinite DC conductivity (or zero electrical resistance). So if you measure the voltage drop across a superconducting wire, you get zero. Alternatively, if you generate a current in a superconducting ring, e.g., by changing the magnetic flux through a ring, the current will persist indefinitely (estimated lifetime $> 10^5$ years).



2. Meissner effect. Above T_C, if you put the metal in an external magnetic field, the field penetrates the metal. Below T_C, the superconductor is a perfect diamagnet and expels the magnetic field. It does this by having a surface current that flows on its surface and screens out the magnetic field. In other words, the surface current produces a magnetic field that cancels out the external magnetic field inside the superconductor.



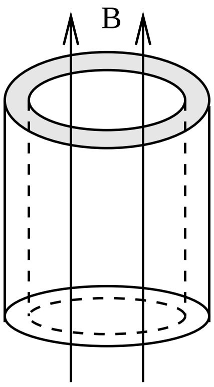
3. Flux quantization. If you put a hollow superconducting cylinder with its z axis parallel to an external magnetic field, then the flux though the hole in the middle is quantized:

$$\Phi = \int \vec{B} \cdot d\vec{A} = n\Phi_o \tag{15}$$

where the "flux quantum" Φ_o is given by

$$\Phi_o = \frac{hc}{2e} \tag{16}$$

If the flux due to the external field does not satisfy the quantization condition, then screening currents will flow in the walls of the cylinder such that the total flux, i.e., that due to both the external field and the screening currents, satisfies the quantization condition. To minimize the screening currents, the system chooses the value of n closest to Φ_{ext}/Φ_o. The flux through the hole in the middle is sometimes called "trapped flux" because it is trapped by the currents flowing in the walls.



4. The thermal conductivity is lousy. A normal metal is a good thermal conductor (that's why your pots and pans are usually made of metal), but below T_C the

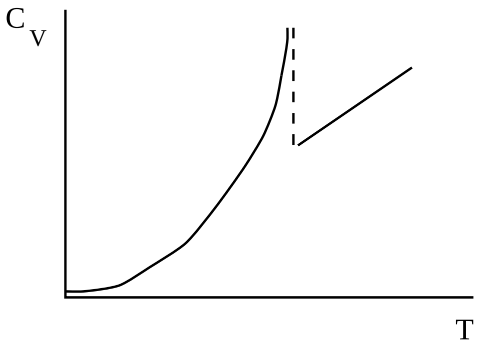
thermal conductivity drops dramatically (usually exponentially). Recall that a superfluid does the opposite and becomes a very good thermal conductor below T_C.

5. Specific heat. In the normal metal above T_C, the specific heat is linear in the temperature:

$$C_V(T) = \gamma T \qquad\qquad T > T_C \tag{17}$$

At T_C there is a jump in the specific heat. We calculated this jump in our Ginzburg–Landau treatment. Below T_C, the specific heat decreases exponentially with decreasing temperature.

$$C_V(T) \sim e^{-\Delta/k_B T} \qquad\qquad T < T_C \tag{18}$$



T_C can range from as low as ~ 1 mK to ~ 160 K (high temperature superconductor under pressure). ($T_C = 135$ K for hiTc mercury compounds.) For most elements, T_C is a few K. For example aluminum has a $T_C \sim 1$ K, lead has $T_C \sim 7$ K, and niobium has $T_C \sim 9$ K.